Conclusions

The ligands $RN(P(OMe)_2)_2$ (R = Me, Ph) do not appear to be as generally useful as DPM for forming binuclear, A-frame type complexes. With the exception of **9** the only binuclear complexes formed contained a single bridging ligand. Among the mononuclear complexes prepared a number appear to adopt highly fluxional, trigonal-bipyramidal structures as a consequence of the short bite of the chelating ligand. One useful result of this work has been the direct determination of values, some of which are quite large, for $^2J_{P-P}$ between trans-disposed phosphorus atoms in four- and five-coordinate rhodium and iridium complexes.

Acknowledgment. We thank the Tulane University Chemistry Department and the Pennzoil Corp. for financial support, Dr. Marie K. Johnson for collecting the X-ray data on the rhodium complex, and Prof. D. M. Roundhill for helpful discussions.

Registry No. **1**, 112968-94-2; **2**, 112947-29-2; **3**, 112947-31-6; **4**, 112947-33-8; **5**, 112947-35-0; **6**, 112947-37-2; **7**, 112947-39-4; **8**, 112947-41-8; **9**, 112947-43-0; **10**, 112947-45-2; **11**, 112947-47-4; **12**, 112947-49-6; **13**, 112947-51-0; **14**, 112947-53-2; **15**, 112947-55-4; BDPPF, 12150-46-8; $[RhCl(COD)]_2$, 12092-47-6; $[Rh(COD)(DPPE)]ClO_4$, 32799-70-5; $[Rh_2(COD)_2(\mu\text{-}Ph_2PC_4H_2OPPh_2)_2](ClO_4)_2$, 112947-57-6; $[Ir_2(COD)_2(\mu\text{-}Ph_2PC_4H_2OPPh_2)_2]ClO_4)_2$, 112947-59-8; $[Ir(COD)(PPh_3)_2]ClO_4$, 52657-94-0; $[Ir(CO)_3(PPh_3)_2]ClO_4$, 15738-08-6; $[IrCl(COD)]_2$, 12112-67-3; $PhN(P(OMe)_2)_2$, 112947-58-7; $MeN(P(OMe)_2)_2$, 34244-05-8; $P(OMe)_3$, 121-45-9.

Supplementary Material Available: Tables of anisotropic thermal parameters, rms amplitudes of anisotropic displacement, intraligand bond distances and interbond angles, torsion angles, and calculated hydrogen atom positions for **9** and **12** (31 pages); listings of F_o vs. F_c for **9** and **12** (139 pages). Ordering information is given on any current masthead page.

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(49) Ardon, M.; Bino, A.; Cotton, F. A.; Dori, Z.; Kaftory, M.; Reisner, G. *Inorg. Chem.* **1982**, *21*, 1912.

Oxidative Addition of Nitroalkanes to Dinuclear Gold(I) Ylide Complexes. The Characterization by X-ray Crystallography of $Au_2(ylide)_2(NO_2)_2$, a Nitro Complex of Gold(II)

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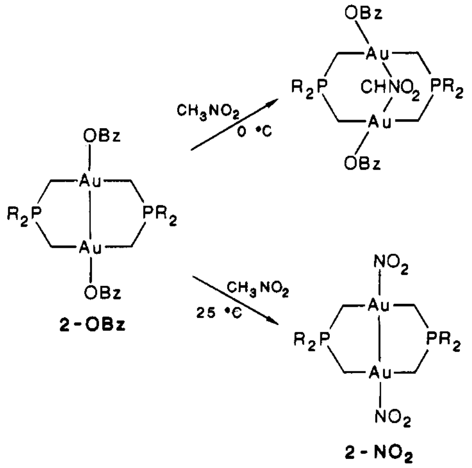
The Au^I ylide complex $[Au((CH_2)_2PPh_2)]_2$ (**1**) reacts oxidatively with nitroalkanes to form a Au^{II} product, $[Au((CH_2)_2PPh_2)NO_2]_2$ (**2-NO₂**). This complex was characterized by IR, NMR, and X-ray crystallography. The identity of the product was confirmed by the quantitative formation of **2-NO₂** from **1** and N_2O_4 "brown gas". The product crystallizes in a monoclinic system $C2/c$: a = 12.159 (2) Å, b = 14.638 (2) Å, c = 16.536 (2) Å, β = 103.757 (11)°, and Z = 4 with R = 0.036 and R_w = 0.033.

Introduction

The two-center oxidative addition chemistry of $[Au((CH_2)_2PPh_2)]_2$ (**1**) is well-established.[1] Reactions with halogens,[2] benzoyl peroxide,[3] and thiuram disulfide[3b] gives symmetrical gold(II)–gold(II) dimers $[Au((CH_2)_2PPh_2)X]_2$ (**2-X**, X = Cl, Br, I, $OC(O)C_6H_5$, SeC_6H_5, etc.). Methyl halides also react[4] with **1** to form metal–metal bonded adducts $[Au((CH_2)_2PPh_2)]_2CH_3X$ (X = I, Br). These studies have revealed that **1** reacts with many solvents.

Our initial studies of reactions of CH_3NO_2 with gold ylide complexes focussed on reactions with the Au^{II} complex $[Au((CH_2)_2PPh_2)OC(O)C_6H_5]_2$ (**2-OBz**). As reported,[3] a nitromethane solution of **2-OBz** at 0 °C produces the A-frame complex wherein $CHNO_2$ bridges two Au(III) centers. At room temperature a somewhat different chemistry takes place. When left standing in a THF/CH_3NO_2 (12:1) solvent mixture, **2-OBz** gives the title compound **2-NO₂**.



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(1) (a) Basil, J. D. Ph.D. Thesis, Case Western Reserve University, Cleveland, OH, 1982. (b) Kaska, W. C. *Coord. chem. Rev.* **1983**, *48*, 1–58. (c) Schmidbaur, H. *Acc. Chem. Res.* **1975**, *8*, 62–70.

(2) (a) Fackler, J. P., Jr.; Basil, J. D. *Inorganic Chemistry, Toward the 21st Century*; Chisholm, M. U., Ed.; ASC Symposium Series 211; American Chemical Society: Washington, DC 1983. (b) Schmidbaur, H.; Franke, R. *Inorg. Chim. Acta* **1975**, *13*, 85–89.

(3) (a) Knachel, H. C.; Dudis, D. S.; Fackler, J. P., Jr. *Organometallics* **1984**, *3*, 1312–1313. (b) Heinrich, D.; Porter, L. C.; Fackler, J. P. Jr., in preparation.

(4) (a) Fackler, J. P., Jr.; Basil, J. D. *Organometallics* **1982**, *1*, 871–873. (b) Fackler, J. P., Jr.; Murray, H. H.; Basil, J. D. *Organometallics* **1984**, *3*, 821–823.

0276-7333/88/2307-0993$01.50/0

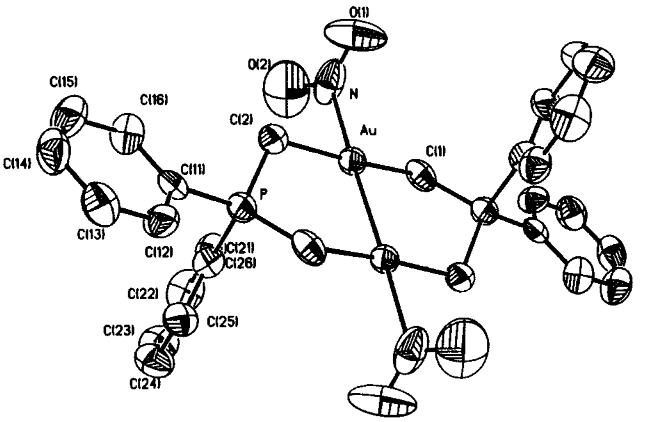

Figure 1. A thermal ellipsoid drawing of $[Au((CH_2)_2PPh_2)NO_2]_2$.

Table I. Crystallographic Data for $[Au((CH_2)_2PPh_2)NO_2]_2$

formula	$Au_2C_{28}H_{28}P_2N_2O_4$
fw	912
space group	$C2/c$
systematic absences	hkl, $h + k = 2n$; $h0l$, $l = 2n$; $0k0$, $2n$
a, Å	12.159 (2)
b, Å	14.638 (2)
c, Å	16.536 (2)
α, deg	90.00
β, deg	103.75 (1)
γ, deg	90.00
V, Å^3	2858.8 (6)
Z	4
d_{calcd}, g cm^{-3}	2.120
cryst size, mm	0.15 × 0.20 × 0.35
$F(000)$, e	1720
μ(Mo Kα), cm^{-1}	103.71
radiatn	monochromated in Mo Kα (λ = 0.71073 Å) incident beam
orientatn reflctns, no., range (2θ)	25, $20 < \theta < 30°$
temp, °C	22
scan method	Ω
data collectn range, 2θ, deg	3, 50
total reflctns measd	5706
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	2528, 1516
check reflctns	3 every 97
no. of parameters refined	100
trans. factors, max, min	0.96, 0.54
R^a	0.036
R_w^b	0.033
goodness-of-fit indicator^c	1.082
largest shift/esd, final cycle	0.022
largest peak, e/Å^3	0.90
g	0.000 28

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = \sum w^{1/2}(|F_o| - |F_c|)/\sum w^{1/2}F_o$; $w^{-1} = [\sigma^2|F_o| + |g|F_o^2]$. ^{c}Goodness-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$.

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for $[Au((CH_2)_2PPh_2)NO_2]_2$

atom	x	y	z	U^a
Au	1552 (1)	2908 (1)	4669 (1)	40 (1)
P	1628 (3)	800 (2)	4168 (2)	39 (1)
N	−56 (10)	3550 (8)	4197 (8)	74 (5)
O(1)	−636 (9)	3821 (8)	4626 (8)	120 (6)
O(2)	−354 (12)	3581 (9)	3425 (10)	139 (7)
C(1)	2241 (10)	4211 (7)	4941 (7)	47 (5)
C(2)	709 (9)	1669 (7)	4305 (8)	45 (5)
C(11)	903 (9)	−295 (7)	3994 (7)	37 (4)
C(12)	1469 (10)	−1098 (7)	4320 (8)	51 (5)
C(13)	914 (12)	−1931 (9)	4150 (9)	61 (6)
C(14)	−167 (12)	−1984 (10)	3666 (8)	63 (6)
C(15)	−737 (12)	−1189 (10)	3345 (8)	62 (6)
C(16)	−218 (11)	−357 (8)	3506 (7)	49 (5)
C(21)	2185 (9)	996 (7)	3265 (7)	40 (4)
C(22)	2906 (11)	329 (9)	3092 (7)	51 (5)
C(23)	3355 (12)	448 (9)	2381 (8)	65 (6)
C(24)	3073 (11)	1196 (11)	1897 (8)	67 (6)
C(25)	2373 (13)	1842 (9)	2077 (9)	66 (6)
C(26)	1922 (10)	1746 (8)	2762 (8)	51 (5)

^{a} Equivalent isotropic U defined as one-third of the trace of the orghogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Bond Lengths (Å) for $[Au((CH_2)_2PPh_2)NO_2]_2$

Au–N	2.142 (11)	Au–C(1)	2.088 (10)
Au–C(2)	2.100 (11)	Au–Au$_a$	2.596 (1)
P–C(2)	1.743 (12)	P–C(11)	1.818 (11)
P–C(21)	1.803 (13)	P–C(1a)	1.761 (11)
N–O(1)	1.181 (20)	N–O(2)	1.242 (20)

Table IV. Selected Bond Angles (deg) for $[Au((CH_2PPh_2)NO_2]_2$

N–Au–C(1)	87.9 (4)	N–Au–C(2)	86.2 (4)
C(1)–Au–C(2)	173.7 (4)	An–Au–Au$_a$	175.9 (4)
C(1)–Au–Au$_a$	93.4 (3)	C(2)–Au–Au$_a$	92.7 (3)
C(2)–P–C(11)	111.2 (5)	C(2)–P–C(21)	111.7 (6)
C(11)–P–C(21)	105.9 (5)	C(2)–P–C(1a)	107.1 (6)
C(11)–P–C(1a)	112.2 (5)	C(21)–P–C(1a)	108.8 (6)
Au–N–O(1)	123.5 (10)	Au–N–O(2)	114.1 (11)
O(1)–N–O(2)	122.3 (13)	Au–C(1)–P$_a$	111.5 (5)
Au–C(2)–P	112.6 (6)		

It is known[3] (by ^{31}P NMR) that the reaction of **2-OBz** with CH_3NO_2 gives **1** as one of the byproducts. In weakly acidic media, compound **1**, benzoic acid, and other products result from **2-OBz**. In order to begin to understand various aspects of this complex reaction, **1** was reacted directly with nitromethane and other nitroalkanes.

Reactions of Cu^I complexes with nitroalkanes[5] and dimethylformamide[6] DMF have been known for many years. In these solvents Cu^I is oxidized by oxygen to Cu^{II}. With nitroalkanes the product is an N-bonded copper(II) nitrate. Several other metal-catalyzed oxidations involving nitro compounds are well-established.[7]

This paper describes the reaction of **1** with nitroalkanes and the structure of the product obtained with CH_3NO_2, the first example of a Au(II) nitro complex.

Experimental Section

X-ray Crystallography. Intensity data for $[Au((CH_2)_2PPh_2)NO_2]_2$ were collected on the Nicolet R3m/E system. A crystal (0.10 mm × 0.15 mm × 0.35 mm) was mounted on a glass fiber and optically aligned in the beam. Cell constants were obtained from 25 high-angle reflections ($20° < 2\theta < 30°$). Reflection conditions (hkl, $h + k = 2n$; $h0l$, $l = 2n$; $0k0$, $k = 2n$) indicate $C2/c$ or Cc space group. $C2/c$ (No. 15) was confirmed by successful refinement. The SHELXTL package installed on the Data General Eclipse S140 computer was used. Decay, Lorentz, polarization, and empirical absorption corrections were applied. The position of the gold atom was located from the direct methods (SOLV). Coordinates of all the other non-hydrogen atoms were found from the successive least-squares refinements and difference Fourier maps. Hydrogen atom positions were calculated according to sp^2 or sp^3 hybridization and fixed at 0.96 Å from C. All non-hydrogen atoms were refined anisotropically.

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(5) Garland, M. T.; Spondie, E.; Zamudio, W. *J. Appl. Cryst.* **1981**, *14*, 475–477.

(6) Salazar, J.; Baraona, R.; Zamudio, W. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2881.

(7) (a) Andrews, M. A.; Cheng, T. C.-T.; Cheng, C.-W. F.; Kelly, K. P. *Organometallics* **1984**, *3*, 1777–1785. (b) Okomoto, T.; Oka, S. *J. Chem. Soc., Chem. Commun.* **1984**, 289.

Final refinement of 100 parameters gave $R = 0.0364$ and $R_w = 0.0331$. The largest residual peak was 0.9 e/Å^3.

Synthesis. The reagent grade nitroalkanes and the deuteriated NMR solvents were dried over molecular sieves. Gold label nitromethane, Aldrich (impurities suggested by GC 0.6%), and distilled nitromethane and nitrobenzene were tried initially, but no differences in reactivity were observed. *p*-Nitrotoluene from Aldrich was used without further purification. The purity of *p*-nitrotoluene was checked by melting point. Fresh THF, distilled over Na/benzophenone, was always used.

Preparation of $[Au((CH_2)_2PPh_2)NO_2]_2$ from Reactions with Nitroalkanes. In a large excess (20 mL) of nitroalkane, 20 mg of 1 was dissolved. When the mixture was left standing in air, for varying lengths of time, CH_3NO_2 about 3 weeks, $CH_3CH_2NO_2$ about 2 days, $(CH_3)_2CHNO_2$ about 3 weeks, and $CH_3CH_2CH_2NO_2$ about 2 weeks, the color changed from green to intense orange. With $CH_3CH_2NO_2$ a yellow precipitate appeared (84% yield). The solvent was allowed to evaporate slowly, and orange crystals were formed (yield ~50%). Crystals of X-ray quality obtained by dissolving **2-NO$_2$** in chloroform and slowly evaporating the solvent; mp 216.5 °C. Anal. Calcd for $Au_2H_{28}P_2N_2O_4$: C, 36.84; H, 3.07; N, 3.07. Found: C, 36.90; H, 3.02; N, 3.01. ^{1}H NMR ($CDCl_3$); δ 7.45 and 7.65 (m, phenyl protons), 1.87 (d, $J_{P-H} = 9.9$ Hz, CH_2).

Preparation of $[Au((CH_2)_2PPh_2)NO_2]_2$ from Reaction with N_2O_4 "Brown Gas". In a 25-mL Schlenk flask 25 mg of 1 was suspended in 5 mL of toluene. This flask was degassed and connected via cannula to a three-necked round-bottomed flask containing about 5 mL of (concentrated) nitric acid. An outlet needle was inserted in the stopper on the 25-mL Schlenk flask. Ethanol (95%) was slowly added to the nitric acid by syringe, approximately 0.5-mL total over a period of 30 min. The brown gas, containing N_2O_4, was bubbled through the suspension of 1, producing a yellow precipitate (90% yield). The identification of this compound as **2-NO$_2$** was confirmed by its melting point.

Preparation of $[Au((CH_2)_2PPh_2)(NO_2)]_2$ from the Reaction of 1 and *p*-Nitrotoluene in THF. To a stirred solution of 1, 30 mg (0.036 mmol) in THF (10 mL), was added *p*-nitrotoluene (0.01 g, 0.072 mmol) in one portion at room temperature. The resultant reaction mixture was stirred several days (15–20 days). During this time an orange-yellow solid precipitated. After separation of solid, **2-NO$_2$**, by filtration, the organic products from the filtrate were extracted with diethyl ether. The Et_2O layer was washed with water (10 mL, twice) and dried with $MgSO_4$. The solvent was evaporated to dryness yielding a viscous yellow liquid. The liquid was purified by preparative TLC (silica/40% EtOAc in hexane) and was found to contain toluene and polymerized THF. ^{1}H NMR of yellow liquid in $CDCl_3$; δ 7.2 (m, 5 H, phenyl protons), 2.3 (s, 3 H, CH_3) assigned for toluene; 5.65 (d, $J = 10$ Hz, 1 H, olefinic protons), 4.3 (m, 2 H, olefinic protons), 4.1 (m, 1 H, 4-H), 4.0 (m, 3-H), 2.1–1.9 (br m, 5-H) assigned for oligomerized THF. MS (electron impact): *m/e* 92 (M$^+$, toluene), 210 (M$^+$, oligomerized product of THF). The purity of the orange yellow Au^{II} complex obtained from this reaction was checked by ^{1}H NMR and mixed melting point with authentic material.

Physical Measurements. The NMR spectra were obtained in the $CDCl_3$ (TMS reference) or THF-d_8 solutions by using Varian Instruments EM390 (90 MHz) and XL-200 (200 MHz) spectrometers.

IR spectra were obtained with IBM FTIR/85 and Perkin-Elmer 783 infrared spectrometers. Samples were prepared as CsI solid pellets. Elemental analysis were performed by Galbraith Laboratories Inc.

Results

Upon reaction of 1 with nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane, an orange-yellow product is formed. Long reaction times are required (a few days to several weeks), depending on the nitroalkane and on the concentration of the gold complex. Once the product was isolated, it is sufficiently stable for characterization. It decomposes in air in a few weeks. Reaction with nitrotoluene in THF gives interesting observations. If the reaction is stirred for about 2 days in diffuse light, no color change is observed. In light the solution color changes to orange color within a few hours. This observation suggested that the reaction is light-sensitive and probably free radical in nature.

The ^{1}H NMR spectra of the title compound **2-NO$_2$** and $[Au((CH_2)_2PPh_2)Cl]_2$ (**2-Cl**) show similar chemical shifts in $CDCl_3$, for the phenyl and methylene protons. This observation is due to the very similar electron-withdrawing properties of Cl and NO_2. The ^{1}H NMR clearly indicated that **2-NO$_2$** is a Au^{II}–Au^{II} dimer.

The formation of **2-NO$_2$** from 1 was followed by ^{1}H NMR. The solubility of 1 in pure nitroalkanes is too low to observe an NMR signal; thus a different solvent system was required. When 5 mg of 1 was dissolved in 0.5 mL of $CDCl_3$ and a 10-fold excess (3.3 μL) of CH_3NO_2 was added, no reaction was observed within the first 24 h. The experiment was repeated with a 100-fold excess of CH_3NO_2. Initially no reaction was observed. When the mixture was left standing overnight, a green flocculent and later polymeric precipitate appeared but the solution NMR spectra showed only the starting materials. Similar results were obtained in $CDCl_3$ with a 10- and a 100-fold excess of $CH_3CH_2NO_2$. The solution was observed by ^{1}H NMR for up to 1 week.

In 0.5 mL of THF only about 3 mg of 1 could be dissolved. A twofold excess of CH_3NO_2 showed by ^{1}H NMR a reaction forming an asymmetrical gold product (two doublets at $\delta(CH_2)$ 1.89 ($J_{PH} = 12.4$ Hz) and $\delta(CH_2)$ 1.29 ($J_{PH} = 12.6$ Hz)). A peak slightly shifted from the CH_3NO_2 (δ 4.32) at δ 4.11 appeared also. Only about two-thirds of the Au^I ylide starting material (δ 1.22 ($J_{PH} = 12.4$ Hz)) was used up in the reaction in the first 2 h. No visible progress was observed after 2 h, but the reaction did seem to go to completion in about 3 months.

Solid pellet CsI IR spectra of **2-NO$_2$** obtained both from CH_3NO_2 and $(CH_3)_2CHNO_2$ were compared to the spectra of 1 and **2-Cl**. All high-frequency bands present in **2-Cl** were also present in **2-NO$_2$**. In the nitroalkane addition product two additional bands, assigned to asymmetric and symmetric vibrations of the NO_2 group, were present at 1262 and 1600 cm^{-1}. These positions are similar to bands found[8] in nitroalkanes as expected since gold has nearly the same electronegativity as carbon. X-ray crystallography shows the title compound on a center of symmetry. The Au–Au bond is very short, 2.596 (1) Å, while the Au–N bond distance, 2.14 (1) Å, is comparable to the Pt–N distance in PtNO$_2$ complexes.[9] The eight-membered ring containing the two metal atoms is in the sterically preferred chair configuration. The average gold carbon bond is 2.1 Å long, a normal distance for Au^{II} ylide[11] complexes.

Since there was an initial question crystallographically as to whether $-NO_2$ or $-N(O)CH_3$, was coordinated to the Au in **2-NO$_2$** formed from CH_3NO_2, both models were refined. The two possibilities were found to be indistinguishable. The N–O bond lengths (or N–O and N–C) are 1.18 (2) and 1.24 (2) Å, but this difference is not statistically significant. It is also not unusual, however, for the two N–O distances in coordinated NO_2 to be somewhat different.[10] The ^{1}H NMR spectrum as well as the synthesis of **2-NO$_2$** using N_2O_4 settled any crystallographic ambiguity.

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[8] (a) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; 3rd ed.; Wiley: New York, 1978. (b) Silverstine, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981.

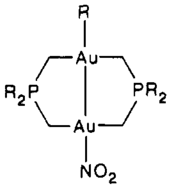
[9] Hedden, D.; Roundhill, D. M.; Walkinshaw, M. D. *Inorg. Chem.* **1985**, *24*, 3146–3150.

[10] Hitchman, M. A.; Rowbottom, G. L. l. *Coord. Chem. Rev.* **1982**, *42*, 55–132.

Discussion

In view of the ease of oxidation[11] of **1**, it is not surprising that it reacts with nitroalkanes and N_2O_4 "brown gas". The symmetrical addition of N_2O_4 is analogous to the oxidative addition of halogens or pseudohalogens to **1**. The product formed is the symmetrical Au^{II}–Au^{II} species, not a mixed-valent Au^{III}–Au^{I} species.

The reaction of nitroalkanes with **1** to form **2-NO$_2$** in some ways appears similar to the oxidative addition observed with alkyl halides. However, no adduct, **3**, has been isolated. Presumably either such an intermediate is not formed or it is destroyed as it is formed.



3

Nitroalkanes support radical reactions; therefore, we believe that a radical[12] chain process forms the stable dinitro product **2-NO$_2$** and various other organic components of alkyl or aryl radicals. Our data have substantiated a radical reaction for **1** with *p*-nitrotoluene in THF. This reaction produces **2-NO$_2$** as a main product with organic radical products including toluene and oligomerized THF. The organic products have been characterized by GC, GC–mass spectrometry, and NMR spectroscopy.

Several possible reaction sequences involving radical formation can be written. One such scheme is shown below. With *p*-nitrotoluene, termination gives toluene as a major organic product. This type of stable arene formation from an aryl radical in a protic solvent[13a] is very common. The THF radical formed by H atom abstraction can undergo a coupling reaction[13b,c] with additional THF or available radicals. The coupling reaction between THF radicals produces oligomerized products.

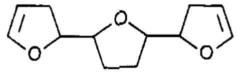
Possible Radical Reaction Sequence

$$RNO_2 + 1 = R^{\bullet} + Au_2NO_2^{\bullet}$$

$$Au_2NO_2^{\bullet} + RNO_2 = R^{\bullet} + Au_2(NO_2)_2 \text{ product}$$

$$R^{\bullet} + \text{THF} \rightarrow \text{THF oligomers} + RH$$

The structure of one oligomerized THF product assigned on the basis of mass and NMR spectroscopy is shown as **a**.



a

Additional evidence for the radical nature of the reaction of **1** with nitroalkanes relates to the nature of the R group. Nitroethane reacts more rapidly than CH_3NO_2 and the other alkyl nitrates studied. This observation is consistent with a radical process with an initiation step which follows the order R = Et > R = Me. Nucleophilic oxidative addition should show reactivity,[14] CH_3 > Et > secondary alkyls, paralleling reactivities observed with alkyl halide additions to **1**, an order different from the one formed here. The alkyl halides addition reaction also is reversible while alkyl and aryl nitrates react irreversibly.

Acknowledgment. The National Science Foundation CHE-8708625 has supported this work. Funding also has been received from the Welch Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Texas A&M Center for Energy and Minerals Research.

Registry No. 1, 81457-56-9; **2-NO$_2$**, 113008-27-8; CH_3NO_2, 75-52-5; $CH_3CH_2NO_2$, 79-24-3; $(CH_3)_2CHNO_2$, 79-46-9; $CH_3CH_2CH_2NO_2$, 25322-01-4; N_2O_4, 10544-72-6; *p*-nitrotoluene, 99-99-0.

Supplementary Material Available: Complete listings of atomic coordinates and isotropic and anisotropic thermal parameters for complex **2-NO$_2$** (2 pages); a table of observed and calculated structure factors for complex **2-NO$_2$** (9 pages). Ordering information is given on any current masthead page.

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[11] Basil, J. D.; Murray, H. H.; Fackler, J. P., Jr.; Tocher, J., Mazany, A. M.; DeLord, T. J.; Trzcinska Bancroft, B.; Knachel, H.; Dudis, D. S. *J. Am. Chem. Soc.* **1985**, *107*, 6908–6915.

[12] Cary, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*; Plenum: New York, 1977; p 552.

[13] (a) Kochi, J. K. *J. Am. Chem. Soc.* **1957**, *79*, 2942–2948. (b) Kochi, J. K. *J. Am. Chem. Soc.* **1962**, *84*, 2121–2127. (c) Stille, J. K.; Cassidy, P.; Plummber, L. *J. Am. Chem. Soc.* **1963**, *85*, 1318–1321.

[14] Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*, Brooks/Cole Publishing Co.: Monterey, CA, 1985; p 174.

[15] Fackler, J. P., Jr.; Murray, H. H.; Trzcinska-Bancroft, B. *Organometallics* **1985**, *4*, 1633–1637.